

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 07-181991

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(22)Date of filing : 18.07.1995

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## (54) DIPPING COATING MATERIAL

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a dipping coating material improved in both mechanical strength and curability while retaining its resin content, thus extremely suitable for electrical and electronic parts, essentially containing an aniline-modified phenolic resin and an epoxy resin.

SOLUTION: This coating material essentially contains (A) an anilinemodified phenolic resin and (B) an epoxy resin (pref. cresol novolak-type epoxy resin  $\leq 500$  in epoxy equivalent). The component A is obtained, in general, by reaction between a phenolic compound and an aldehyde in the presence of aniline and a divalent metal oxide or hydroxide. It is preferable that the aniline modification rate is 0.1-0.4mol per mol of the phenolic compound. Normally, the resin, the component A and the component B account for 5-50wt.%, 3-25wt.%, and 2-25wt.% of the whole coating composition, respectively. The weight ratio A/B is normally 100: (40-140). Besides, it is preferable that this coating material also contain silica as filter and a coupling agent.

*2 globular*

## LEGAL STATUS

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AN 1997:250136 CAPLUS  
 DN 126:226575  
 ED Entered STN: 17 Apr 1997  
 TI Aniline-modified phenolic resins for dipping coatings  
 IN Oochi, Susumu  
 PA Sumitomo Durez Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 4 pp.  
 CODEN: JKXXAF

DT Patent  
 LA Japanese  
 IC ICM C09D163-00  
 ICS C09D005-25; C09D161-34  
 CC 42-9 (Coatings, Inks, and Related Products)  
 Section cross-reference(s): 76

FAN.CNT 1

| PATENT NO.          | KIND | DATE     | APPLICATION NO. | DATE     |
|---------------------|------|----------|-----------------|----------|
| JP 09031406         | A2   | 19970204 | JP 1995-181991  | 19950718 |
| PRAI JP 1995-181991 |      | 19950718 |                 |          |

CLASS

| PATENT NO.  | CLASS | PATENT FAMILY CLASSIFICATION CODES |
|-------------|-------|------------------------------------|
| JP 09031406 | ICM   | C09D163-00                         |
|             | ICS   | C09D005-25; C09D161-34             |

AB The coatings, having good storage stability, and useful for elec. and electronic devices, contain aniline-modified phenolic resins, and epoxy resins. (Thus, a resol (prepared from phenol 100, 37%-formalin 150, and aniline 30 parts) 10, epoxy o-cresol novolak resin 10, and crystalline silica 80 parts were mixed and cured at 120° to give a test piece having hardness 86, and 85, initially, and after dipping in acetone for 2 h, resp.

ST dipping coating aniline modified phenolic resin; epoxy resin silica dipping coating; storage stability dipping coating phenolic resin; electronic device epoxy dipping coating

IT Coating materials  
 Electric apparatus

(dipping coatings containing aniline-modified phenolic resins and epoxy resins)

IT Phenolic resins, uses

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(dipping coatings containing aniline-modified phenolic resins and epoxy resins)

IT Phenolic resins, uses

RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(epoxy, o-cresol novolak; dipping coatings containing aniline-modified phenolic resins and epoxy resins)

IT Epoxy resins, uses

RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(phenolic, o-cresol novolak; dipping coatings containing aniline-modified phenolic resins and epoxy resins)

IT 7631-86-9, Silica, uses

RL: MOA (Modifier or additive use); USES (Uses)

(crystalline; dipping coatings containing aniline-modified phenolic resins

and

epoxy resins)

IT 24937-74-4P, Aniline-formaldehyde-phenol copolymer

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(dipping coatings containing aniline-modified phenolic resins and epoxy resins)

DERWENT-ACC-NO: 1997-161755

DERWENT-WEEK: 199715

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TITLE: Dip coating compsn. for electronic and electrical parts  
- contg. aniline modified phenol! resin epoxy! resin and  
opt. silica

PATENT-ASSIGNEE: SUMITOMO DULEZ KK[SUMN]

PRIORITY-DATA: 1995JP-0181991 (July 18, 1995)

PATENT-FAMILY:

| PUB-NO               | PUB-DATE         | LANGUAGE | PAGES | MAINIPC     |
|----------------------|------------------|----------|-------|-------------|
| <u>JP 09031406 A</u> | February 4, 1997 | N/A      | 004   | C09D 163/00 |

APPLICATION-DATA:

| PUB-NO       | APPL-DESCRIPTOR | APPL-NO       | APPL-DATE     |
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| JP 09031406A | N/A             | 1995JP0181991 | July 18, 1995 |

INT-CL (IPC): C09D005/25, C09D161/34 , C09D163/00

ABSTRACTED-PUB-NO: JP 09031406A

BASIC-ABSTRACT:

A dipping coating compsn. (P) contains aniline modified phenol resin (A) epoxy resin (B) and opt. silica (C).

USE - (P) is suitable for dip coating electronic and/or electrical parts.

ADVANTAGE - (P) has good curing property and cured coating exhibits good mechanical strength.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: DIP COATING COMPOSITION ELECTRONIC ELECTRIC PART CONTAIN ANILINE  
MODIFIED POLYPHENOL RESIN POLYEPOXIDE RESIN ETION SILICA

DERWENT-CLASS: A21 A82 G02 L03 V04 X12

CPI-CODES: A05-B; A05-C01B1; A08-D; A11-B05A; A12-E01; G02-A02F; G02-A02G;  
G02-A05B; L03-J;

EPI-CODES: V04-X01B; X12-E02B;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1278U; 2020U

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; P0464\*R D01 D22 D42 F47 ; P0497 P0464 P0226 P0282 M2175 D01

D18 ; M9999 M2073

Polymer Index [1.2]

018 ; ND01 ; K9449 ; N9999 N7045 N7034 N7023 ; N9999 N7147 N7034

N7023 ; K9483\*R ; K9712 K9676 ; B9999 B4988\*R B4977 B4740 ; B9999

B4091\*R B3838 B3747 ; Q9999 Q7114\*R ; Q9999 Q7330\*R

Polymer Index [1.3]

018 ; A999 A157\*R

Polymer Index [1.4]

018 ; A999 A146

Polymer Index [1.5]

018 ; A999 A248\*R

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2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the very suitable dipping coating for paint of the electrical and electric equipment and electronic parts.

[0002]

[Description of the Prior Art] The electrical and electric equipment and electronic parts have many to which sheathing is performed by resist for the purpose of the protection from moisture, and mechanical protection. The property of this resist has big effect on the resistance to humidity of direct components, and a mechanical property. There are a solvent system dip coating method, a casting method, a fine-particles sheathing method, the fabricating method, etc. in the covering approach of these components. Among these, after a solvent system dip coating method is immersed in the coating which the solvent was made to carry out dissolution distribution of fillers, such as a silica and a calcium carbonate, the other additives, etc., and obtained thermosetting resin, such as phenol resin and an epoxy resin, in components and evaporates a solvent at a room temperature, it is the approach of carrying out heat hardening processing and covering components.

[0003] The coating used with a solvent system dip coating method, i.e., a DIPPIINGU coating, contains the filler so much, and generally the hardening paint film has a small coefficient of thermal expansion at the shape of porous one, and is excellent in thermal shock resistance. Solvent system DIP coat material has the outstanding heat-resistant impact property as a sheathing material which covers the loading circuit boards, such as chip coat material which carries out subcovering of the resin sealing agent especially in the hybrid IC field, i.e., the semiconductor chip etc., or mold components, and the amount used is increasing.

[0004]

[Problem(s) to be Solved by the Invention] Since a dipping coating has much blending ratio of coal of a filler and there are few pitches, the blemish was weakly attached simply by the paint film, and a crack tended to enter. When \*\*\*\*\* made [ increasing a pitch / more ] the pitch for the improvement of a paint film on the strength than 30 % of the weight, coefficient of thermal expansion increased, thermal-shock-resistance ability fell extremely, and there was that sufficient effectiveness is not acquired by the actual condition.

[0005] Moreover, use of a weak component and an ingredient is also increasing with heat with the miniaturization of an electron and electrical machinery components, and diversification. Although the quantity of the hardening accelerator in a coating is increased, and the hardenability in low temperature is given or a 2 liquid type coating may be used since the weak ingredient of such thermal resistance is covered, a price is expensive, or pot life (working life) and shelf life are shortened, the fault of worsening the paint film appearance in which workability is reduced appears, and it has not resulted in the essential improvement.

[0006] While the pitch had maintained a small coefficient of thermal expansion below by 30% weight, it was anxious for the DIPPIINGU coating which has sufficient reinforcement and can be hardened at low

temperature. This invention improves the reinforcement and hardenability of the phenol resin system dipping coating in which reinforcement is generally inferior, with the conventional pitch maintained.

[0007]

[Means for Solving the Problem] the dipping coating with which this invention contains aniline denaturation phenol resin and an epoxy resin as an indispensable component -- it is -- desirable -- as a filler -- a silica -- further -- as an additive -- a coupling agent -- yes, it is the dipping coating which it comes to obtain. By considering as such a presentation, it excels in hardenability and a dipping coating with the good reinforcement of a paint film can be obtained.

[0008]

The aniline denaturation resol in this invention is phenol resin indicated by JP,58-109525,A, namely, is an aniline denaturation resol obtained in phenols and aldehydes in response to the bottom of existence of the oxide of an aniline and divalent metal or a hydroxide. In an aniline denaturation resol, although the range of the rate of denaturation of an aniline is 0.05-0.5 mols to one mol of phenols, its 0.1-0.4 mols are desirable in respect of the ease of resin manufacture, and the fast curability of a DIPINGU coating. The loadings of this aniline denaturation resol are usually 3 - 25% of the weight of the whole coating constituent.

[0009]

If the epoxy resin used in this invention is a solid epoxy resin which has at least two epoxy groups in 1 molecule, it is limited especially and has \*\*\*\*, for example, the bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, an aliphatic series glycidyl ether mold epoxy resin, a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, cycloaliphatic epoxy resin, a bromine-ized epoxy resin, various modified epoxy resins, etc. In this, a 500 or less weight per epoxy equivalent thing is desirable. these epoxy resins -- the inside of a coating constituent -- one sort -- or it is blended two or more. In an epoxy resin, things desirable type are a novolak mold epoxy resin, especially a cresol novolak mold epoxy resin, and reinforcement and its hardenability improve with sufficient balance.

[0010] The rate of an epoxy resin to the whole constituent is usually 2 - 25 % of the weight. The rate of an epoxy resin to the aniline denaturation phenol resin 100 weight section is the 40 - 140 weight section. Under in 40 weight sections, if there is [ rather than is enough ] the improvement in on the strength of a coating than the 140 weight sections, adhesion with a base material will fall. [ more ] The rate of the pitch to the whole constituent is usually 5 - 50 % of the weight. If reinforcement is small when fewer than 5 % of the weight, and 50 % of the weight is exceeded, coefficient of thermal expansion will become large and thermal shock resistance will come to fall.

[0011]

It is thought that the reason which the dipping coating of this invention has fast curability, namely, a coating can harden in low temperature and a short time is because the reaction of an aniline denaturation resol and an epoxy resin is promoted since the aniline molecule part in an aniline denaturation resol has basicity. Furthermore, the resin hardened material to which these reacted has large bonding strength, and it becomes the thing excellent in reinforcement.

[0012]

In this invention, preferably, in order to raise reinforcement more, a silica is blended as a filler. A silica has a crystal silica, fused silica, etc., it has the shape of the letter of crushing, a globular shape, a grain, and hollow etc., and the configuration may be used suitably and two or more sorts of silicas which carried out coupling agent processing may also use these silicas for them, mixing. The rate to the whole constituent of a silica is usually 50 - 95 % of the weight, and can also be used together with the filler represented by other calcium carbonates, the aluminum hydroxide, etc. [0013] Still more preferably, in order to strengthen compatibility, such as bonding strength of resin and a filler, wettability, and adhesion, a coupling agent is used for this invention. There is a silane system coupling agent, a titanate system coupling agent, or an aluminate coupling agent in a coupling agent, and 0.01-5.0 weight section combination is usually carried out to the whole coating constituent for the above-mentioned purpose.

[0014] although the dipping coating of this invention carries out dissolution distribution at a solvent in the case of use -- the solvent -- one sort of solvents, such as ketones, such as alcohols solvents, such as hydrocarbon system solvents, such as toluene and a xylene, a methanol, and ethanol, an acetone, and a methyl ethyl ketone, other ester systems, an ether system, a ether alcohol system, and an ether ester system, or two sorts or more -- optimum dose (it changes with service conditions) -- 5-40 weight section combination use is preferably carried out to the constituent 100 weight section.

[0015] Optimum dose combination of the phosphorus compound system hardening accelerator which makes representation the nitride which makes an imidazole derivative representation, and triphenyl phosphine, the fire-resistant assistant which makes an antimony trioxide representation, other leveling agents, a defoaming agent, a pigment, and the color can be carried out at this invention if needed.

[0016]

[Example] This invention is not limited by the example although an example explains this invention to a detail below. The "weight section" and "% of the weight" are shown the "section" and all "%" indicated below.

[0017] (1) As the combination example 1 phenol 100 section of a coating, the 37% formalin 150 section, the aniline 30 section, and a catalyst, the magnesium-hydroxide 3 section was taught to the agitator and the reaction vessel equipped with the reflux condenser, and carried out the temperature up to 70 degrees C, and it maintained at this temperature for 90 minutes. Subsequently, it heated under the vacuum and dehydration and a de-free phenol were performed. When the melting point of resin amounted to 85 degrees C, it discharged and quenched from the reaction vessel, and solid resol mold aniline denaturation phenol resin (it considers as an aniline denaturation resol [1] hereafter) was obtained. The aniline denaturation resol [1] 10 section, the epoxy orthochromatic cresol novolak 10 section, the crystal silica 80 section, an acetone pair methanol = the silane coupling agent 2 section was mixed with combination and an agitator as the partially aromatic solvent 20 section of 3 to 1, and an additive for 2 hours, and the coating was produced. Furthermore, it diluted with the above-mentioned partially aromatic solvent, and the viscosity in 25 degrees C was adjusted to 1.5 Pa-s.

[0018] After it taught the zinc hydroxide 4 section to the agitator and the reaction vessel equipped with the reflux condenser and it carried out the temperature up to 90 degrees C as the example 2 phenol 100 section, the 37% formalin 140 section, and a catalyst, small quantity [ every ] dropping addition of the aniline 20 section was carried out over 20 minutes. It was made to react for 30 more minutes, keeping at 90 degrees C. Subsequently, it heated under the vacuum and dehydration and a de-free phenol were performed. When the melting point of resin amounted to 80 degrees C, it discharged and quenched from the reaction vessel, and solid resol mold aniline denaturation phenol resin (it considers as an aniline denaturation resol [2] hereafter) was obtained. The aniline denaturation resol [2] 10 section, the epoxy orthochromatic cresol novolak 10 section, the crystal silica 80 section, an acetone pair methanol = the silane coupling agent 2 section was mixed with combination and an agitator as the partially aromatic solvent 20 section of 3 to 1, and an additive for 2 hours, and the coating was produced. Furthermore, it diluted with the above-mentioned partially aromatic solvent, and the viscosity in 25 degrees C was adjusted to 1.5 Pa-s.

[0019] The example of comparison 1 aniline denaturation resol [1] 20 section, the calcium-carbonate 80 section, an acetone pair methanol = the partially aromatic solvent 25 section of 3 to 1 was mixed with combination and an agitator for 2 hours, and the coating was produced. Furthermore, it diluted with the above-mentioned partially aromatic solvent, and the viscosity in 25 degrees C was adjusted to 1.5 Pa-s.

[0020] The example of comparison 2 aniline denaturation resol [2] 20 section, the calcium-carbonate 80 section, an acetone pair methanol = the partially aromatic solvent 25 section of 3 to 1 was mixed with combination and an agitator for 2 hours, and the coating was produced. Furthermore, it diluted with the above-mentioned partially aromatic solvent, and the viscosity in 25 degrees C was adjusted to 1.5 Pa-s.

[0021] (2) the test piece (about 100x20x2mm) was produced, and it was made to harden on condition that predetermined in the evaluation approach profit \*\*\*\* coatings The hardened test piece was immersed in the acetone after flexural strength measurement (JIS K 7203), measured the surface hardness of 1 and 2 or 3 hours after with the Barcol hardness plan, and made it the index of hardenability.

[0022] (3) As the result result was shown in Table 1, the dipping coating obtained according to examples 1 and 2 hardened enough, and showed the bending strength of 3 times or more in 90 degrees C and 2 hours as compared with the coating by the examples 1 and 2 of a comparison.

[0023]

[Table 1]

| 硬化<br>温度 (℃) | アセトン<br>浸漬(Hr) | 実施例1 |    | 実施例2 |    | 比較例1 |    | 比較例2 |    |
|--------------|----------------|------|----|------|----|------|----|------|----|
|              |                | 曲げ強さ | 硬度 | 曲げ強さ | 硬度 | 曲げ強さ | 硬度 | 曲げ強さ | 硬度 |
| 90           | 0              |      | 85 |      | 88 |      | 45 |      | 50 |
|              | 1              | 20.6 | 85 | 21.3 | 88 | 測定   | 0  | 測定   | 0  |
|              | 2              |      | 85 |      | 86 | 不可   | 0  | 不可   | 0  |
|              | 3              |      | 80 |      | 85 |      | 0  |      | 0  |
| 100          | 0              |      | 85 |      | 88 |      | 88 |      | 78 |
|              | 1              | 33.0 | 85 | 33.6 | 87 | 4.7  | 53 | 2.6  | 64 |
|              | 2              |      | 83 |      | 87 |      | 32 |      | 32 |
|              | 3              |      | 80 |      | 86 |      | 0  |      | 0  |
| 110          | 0              |      | 88 |      | 88 |      | 87 |      | 87 |
|              | 1              | 31.4 | 87 | 33.7 | 88 | 10.2 | 85 | 9.8  | 85 |
|              | 2              |      | 86 |      | 87 |      | 85 |      | 84 |
|              | 3              |      | 85 |      | 86 |      | 85 |      | 82 |
| 120          | 0              |      | 86 |      | 90 |      | 88 |      | 88 |
|              | 1              | 32.4 | 86 | 33.0 | 88 | 10.3 | 87 | 10.5 | 88 |
|              | 2              |      | 85 |      | 87 |      | 86 |      | 87 |
|              | 3              |      | 85 |      | 87 |      | 86 |      | 86 |
| 130          | 0              |      | 87 |      | 90 |      | 89 |      | 88 |
|              | 1              | 35.6 | 86 | 36.7 | 88 | 10.0 | 88 | 10.1 | 88 |
|              | 2              |      | 85 |      | 88 |      | 87 |      | 88 |
|              | 3              |      | 85 |      | 87 |      | 87 |      | 87 |
| 140          | 0              |      | 89 |      | 90 |      | 88 |      | 89 |
|              | 1              | 39.8 | 88 | 41.1 | 90 | 10.6 | 88 | 10.7 | 88 |
|              | 2              |      | 87 |      | 88 |      | 87 |      | 88 |
|              | 3              |      | 86 |      | 88 |      | 86 |      | 87 |

硬度：バーコル硬度 曲げ強さ：単位：N/mm<sup>2</sup>

[0024]

[Effect of the Invention] Since the dipping coating of this invention makes a pitch an aniline denaturation resol and an epoxy resin, is preferably excellent in hardenability a silica and by blending a coupling agent further as a filler and shows good reinforcement, it is very suitable as the electrical and electric equipment and an object for electronic parts.

[Translation done.]

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CLAIMS

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[Claim(s)]

[Claim 1] The dipping coating characterized by containing the following (A) - (B) component as an indispensable component.

(A) Aniline denaturation phenol resin (B) epoxy resin [claim 2] The dipping coating characterized by containing the following (A) - (C) component as an indispensable component.

(A) Aniline denaturation phenol resin (B) epoxy resin (C) silica [claim 3] The dipping coating according to claim 1 or 2 with which the coupling agent is blended.

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[Translation done.]



(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開平9-31406

(43)公開日 平成9年(1997)2月4日

| (51)Int.Cl. <sup>6</sup> | 識別記号 | 庁内整理番号 | F I            | 技術表示箇所 |
|--------------------------|------|--------|----------------|--------|
| C 0 9 D 163/00           | PKH  |        | C 0 9 D 163/00 | PKH    |
| 5/25                     | PQY  |        | 5/25           | PQY    |
| 161/34                   | PHG  |        | 161/34         | PHG    |

審査請求 未請求 請求項の数3 O L (全 4 頁)

|          |                 |         |   |
|----------|-----------------|---------|---|
| (21)出願番号 | 特願平7-181991     | (71)出願人 | 000183277<br>住友デュレズ株式会社<br>東京都品川区東品川2丁目5番8号 |
| (22)出願日  | 平成7年(1995)7月18日 | (72)発明者 | 大内 丞<br>東京都品川区東品川2丁目5番8号 住友<br>デュレズ株式会社内    |

(54)【発明の名称】 ディッピング塗料

(57)【要約】

【構成】 必須成分としてアニリン変性フェノール樹脂とエポキシ樹脂、好ましくは充填材としてシリカ、及びカップリング剤を含有するディッピング塗料。

【効果】 硬化性に優れて、良好な強度を示し、電気・電子部品用として極めて好適である。

## 【特許請求の範囲】

【請求項1】 下記の(A)～(B)成分を必須成分として含有することを特徴とするディッピング塗料。

(A) アニリン変性フェノール樹脂

(B) エポキシ樹脂

【請求項2】 下記の(A)～(C)成分を必須成分として含有することを特徴とするディッピング塗料。

(A) アニリン変性フェノール樹脂

(B) エポキシ樹脂

(C) シリカ

【請求項3】 カップリング剤が配合されている請求項1又は2記載のディッピング塗料。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は電気・電子部品の塗装に極めて好適なディッピング塗料に関するものである。

## 【0002】

【従来の技術】電気・電子部品は湿気からの保護及び機械的保護を目的に絶縁塗料により外装が施されているものが多い。この絶縁塗料の特性は直接部品の耐湿特性、機械的特性に大きな影響を与える。これらの部品の被覆方法には溶剤系ディップコート法、注型法、粉体外装法、成形法などがある。このうち溶剤系ディップコート法は、フェノール樹脂やエポキシ樹脂などの熱硬化性樹脂を、シリカや炭酸カルシウムなどの充填材、及びその他の添加剤等を溶剤に溶解分散させて得た塗料に、部品を浸漬し、室温にて溶剤を蒸発させた後、加熱硬化処理して部品を被覆する方法である。

【0003】溶剤系ディップコート法で使用する塗料、即ち、ディッピング塗料は、多量に充填材を含んでおり、その硬化塗膜は一般にポーラス状で熱膨張率が小さく、耐熱衝撃性に優れている。特にハイブリッドIC分野における樹脂封止材、すなわち半導体チップ等を部分被覆するチップコート材、あるいはモールド部品等搭載回路基板を被覆する外装材として溶剤系ディップコート材は優れた耐熱衝撃特性を有しており、その使用量が増大している。

## 【0004】

【発明が解決しようとする課題】ディッピング塗料は、充填材の配合割合が多く樹脂分が少ないため、塗膜が弱く簡単に傷が付いたり、クラックが入り易かった。塗膜の強度改善のため、樹脂分を増加することが考えられるが、樹脂分を30重量%より多くすると、熱膨張率が増加し、耐熱衝撃性能が極端に低下し、十分な効果が得られないのが実情であった。

【0005】また、電子・電器部品の小型化、多様化に伴い、熱に弱い素子、材料の使用も増えている。これらの耐熱性の弱い材料を被覆するため、塗料中の硬化促進剤を増量し、低温での硬化性を付与する、あるいは2液型の塗料を使用することがあるが、価格が高価であった

り、ポットライフ(可使用時間)や保存性を短くし、作業性を低下させてしまう、塗膜外観を悪化させるなどの欠点が現れ、本質的な改善には至っていない。

【0006】樹脂分が30%重量以下で小さい熱膨張率を保ったまま、十分な強度を有し、かつ低温で硬化可能なディッピング塗料が切望されていた。本発明は、従来の樹脂分を維持したまま、一般に強度の劣るフェノール樹脂系ディッピング塗料の強度と硬化性を改善するものである。

## 10 【0007】

【課題を解決するための手段】本発明は、必須成分としてアニリン変性フェノール樹脂とエポキシ樹脂とを含有するディッピング塗料であり、好ましくは充填材としてシリカを、さらに添加剤としてカップリング剤をはいこうしてなるディッピング塗料である。このような組成とすることにより、硬化性に優れ、塗膜の強度の良好なディッピング塗料を得ることができたものである。

【0008】本発明におけるアニリン変性レゾールとは、特開昭58-109525号公報に開示されたフェノール樹脂であり、即ち、フェノール類とアルデヒド類をアニリンと2価金属の酸化物または水酸化物の存在下に反応して得られるアニリン変性レゾールである。アニリン変性レゾールにおいて、アニリンの変性率はフェノール類の1モルに対して0.05～0.5モルの範囲であるが、0.1～0.4モルが樹脂製造の容易さ、ディッピング塗料の速硬化性の点で好ましい。このアニリン変性レゾールの配合量は、通常塗料組成物全体の3～25重量%である。

【0009】本発明において使用するエポキシ樹脂は、1分子中に少なくとも2個のエポキシ基を有する固形エポキシ樹脂であれば、特に限定されず、例えば、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、脂肪族グリシジルエーテル型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、クレゾールノボラック型エポキシ樹脂、脂環式エポキシ樹脂、プロム化エポキシ樹脂、各種変性エポキシ樹脂などがある。この中で、エポキシ当量500以下のものが好ましい。これらのエポキシ樹脂は塗料組成物中に1種又は2以上配合される。エポキシ樹脂の中で、好ましいタイプのものは、ノボラック型エポキシ樹脂、特にクレゾールノボラック型エポキシ樹脂であり、強度及び硬化性がバランスよく向上する。

【0010】組成物全体に対するエポキシ樹脂の割合は通常2～25重量%である。アニリン変性フェノール樹脂100重量部に対するエポキシ樹脂の割合は40～140重量部である。40重量部未満では塗料の強度向上が十分ではなく、140重量部より多いと基材との密着性が低下する。組成物全体に対する樹脂分の割合は通常5～50重量%である。5重量%より少ないと強度が小さく、50重量%を越えると熱膨張率が大きくなり、耐

熱衝撃性が低下するようになる。

【0011】本発明のディッピング塗料が速硬化性を有する、即ち、塗料が低温、短時間で硬化しうる理由は、アニリン変性レゾール中のアニリン分子部分が塩基性を持つため、アニリン変性レゾールとエポキシ樹脂との反応が促進されるためであると考えられる。更に、これらが反応した樹脂硬化物は結合力が大きく、強度に優れたものとなる。

【0012】本発明において、好ましくは、強度をより向上させるために充填材としてシリカを配合する。シリカは、結晶シリカ、溶融シリカ等があり、その形状は破砕状、球状、粒状、中空状等であり、カップリング剤処理したシリカも好適に使用され、これらシリカを2種以上混合して使用してもよい。シリカの組成物全体に対する割合は通常50～95重量%であり、他の炭酸カルシウム、水酸化アルミニウムなどに代表される充填材と併用することも出来る。

【0013】本発明には、更に好ましくは、樹脂と充填材との結合力、ぬれ性、密着性などの親和性を強化するためカップリング剤を使用する。カップリング剤にはシラン系カップリング剤、チタネート系カップリング剤、又はアルミニウム系カップリング剤等があり、上記目的のために塗料組成物全体に対して通常0.01～5.0重量部配合される。

【0014】本発明のディッピング塗料は、使用の際溶剤に溶解分散するが、その溶剤はトルエン、キシレンなどの炭化水素系溶剤、メタノール、エタノールなどのアルコール系溶剤、アセトン、メチルエチルケトンなどのケトン系溶剤、その他、エステル系、エーテル系、エーテルアルコール系、エーテルエステル系などの溶剤1種又は2種以上を適量（使用条件により異なる）、好ましくは、組成物100重量部に対し5～40重量部配合使用する。

【0015】本発明には、イミダゾール誘導体を代表とする窒素化合物やトリフェニルホスフィンを代表とする燐化合物系硬化促進剤、三酸化アンチモンを代表とする難燃助剤、その他レベリング剤、消泡剤、顔料、染料を必要に応じて適量配合することができる。

【0016】

【実施例】以下本発明を実施例によって詳細に説明するが、本発明は実施例によって限定されるものではない。以下に記載された「部」及び「%」はすべて「重量部」及び「重量%」を示す。

【0017】(1) 塗料の配合

実施例1

フェノール100部と37%ホルマリン150部、アニリン30部、触媒として水酸化マグネシウム3部を攪拌機と環流冷却器を備えた反応釜に仕込み、70℃に昇温し90分間この温度に保った。次いで真空中で加熱し、脱水及び脱遊離フェノールを行なった。樹脂の融点が8

5℃に達した時点で反応釜から排出し急冷して、固形のレゾール型アニリン変性フェノール樹脂（以下、アニリン変性レゾール〔1〕とする）を得た。アニリン変性レゾール〔1〕10部、エポキシオルソクレゾールノボラック10部、結晶シリカ80部、アセトン対メタノール＝3対1の混合溶剤20部、添加剤としてシランカップリング剤2部を配合、攪拌機にて2時間混合し、塗料を作製した。更に上記混合溶剤にて希釈して25℃における粘度を1.5Pa・sに調整した。

【0018】実施例2

フェノール100部と37%ホルマリン140部、触媒として水酸化亜鉛4部を攪拌機と環流冷却器を備えた反応釜に仕込み、90℃に昇温した後アニリン20部を20分かけて少量ずつ滴下添加した。90℃に保ちながら、さらに30分間反応させた。次いで真空中で加熱し、脱水及び脱遊離フェノールを行なった。樹脂の融点が80℃に達した時点で反応釜から排出し急冷して、固形レゾール型アニリン変性フェノール樹脂（以下、アニリン変性レゾール〔2〕とする）を得た。アニリン変性レゾール〔2〕10部、エポキシオルソクレゾールノボラック10部、結晶シリカ80部、アセトン対メタノール＝3対1の混合溶剤20部、添加剤としてシランカップリング剤2部を配合、攪拌機にて2時間混合し、塗料を作製した。更に上記混合溶剤にて希釈して25℃における粘度を1.5Pa・sに調整した。

【0019】比較例1

アニリン変性レゾール〔1〕20部、炭酸カルシウム80部、アセトン対メタノール＝3対1の混合溶剤25部を配合、攪拌機にて2時間混合し、塗料を作製した。更に上記混合溶剤にて希釈して25℃における粘度を1.5Pa・sに調整した。

【0020】比較例2

アニリン変性レゾール〔2〕20部、炭酸カルシウム80部、アセトン対メタノール＝3対1の混合溶剤25部を配合、攪拌機にて2時間混合し、塗料を作製した。更に上記混合溶剤にて希釈して25℃における粘度を1.5Pa・sに調整した。

【0021】(2) 評価方法

得られた塗料で試験片（約100×20×2mm）を作製し、所定の条件で硬化させた。硬化した試験片は、曲げ強度測定（JIS K 7203）後、アセトンに浸漬し、1、2、3時間後の表面硬度をバーコル硬度計で測定し、それを硬化性の指標とした。

【0022】(3) 結果

結果は表1に示したように、実施例1、2により得られたディッピング塗料は90℃、2時間で十分硬化し、比較例1、2による塗料に比較して3倍以上の曲げ強さを示した。

【0023】

【表1】

| 5            |                | 6    |    |      |    |      |    |      |    |
|--------------|----------------|------|----|------|----|------|----|------|----|
| 硬化<br>温度 (℃) | アセトン<br>浸漬(Hr) | 実施例1 |    | 実施例2 |    | 比較例1 |    | 比較例2 |    |
|              |                | 曲げ強さ | 硬度 | 曲げ強さ | 硬度 | 曲げ強さ | 硬度 | 曲げ強さ | 硬度 |
| 90           | 0              |      | 85 |      | 88 |      | 45 |      | 50 |
|              | 1              | 20.6 | 85 | 21.3 | 88 | 測定   | 0  | 測定   | 0  |
|              | 2              |      | 85 |      | 86 | 不可   | 0  | 不可   | 0  |
|              | 3              |      | 80 |      | 85 |      | 0  |      | 0  |
| 100          | 0              |      | 85 |      | 88 |      | 88 |      | 78 |
|              | 1              | 33.0 | 85 | 33.6 | 87 | 4.7  | 53 | 2.6  | 64 |
|              | 2              |      | 83 |      | 87 |      | 32 |      | 32 |
|              | 3              |      | 80 |      | 86 |      | 0  |      | 0  |
| 110          | 0              |      | 88 |      | 88 |      | 87 |      | 87 |
|              | 1              | 31.4 | 87 | 33.7 | 88 | 10.2 | 85 | 9.8  | 85 |
|              | 2              |      | 86 |      | 87 |      | 85 |      | 84 |
|              | 3              |      | 85 |      | 86 |      | 85 |      | 82 |
| 120          | 0              |      | 86 |      | 90 |      | 88 |      | 88 |
|              | 1              | 32.4 | 86 | 33.0 | 88 | 10.3 | 87 | 10.5 | 88 |
|              | 2              |      | 85 |      | 87 |      | 86 |      | 87 |
|              | 3              |      | 85 |      | 87 |      | 86 |      | 86 |
| 130          | 0              |      | 87 |      | 90 |      | 89 |      | 88 |
|              | 1              | 35.6 | 86 | 36.7 | 88 | 10.0 | 88 | 10.1 | 88 |
|              | 2              |      | 85 |      | 88 |      | 87 |      | 88 |
|              | 3              |      | 85 |      | 87 |      | 87 |      | 87 |
| 140          | 0              |      | 89 |      | 90 |      | 88 |      | 89 |
|              | 1              | 39.8 | 88 | 41.1 | 90 | 10.6 | 88 | 10.7 | 88 |
|              | 2              |      | 87 |      | 88 |      | 87 |      | 88 |
|              | 3              |      | 86 |      | 88 |      | 86 |      | 87 |

硬度：パーコール硬度 曲げ強さ：単位：N/mm<sup>2</sup>

【0024】

【発明の効果】本発明のディッピング塗料は、アニリン変性レゾール及びエポキシ樹脂を樹脂分とし、好ましく\*

\*は充填材としてシリカ、更にはカップリング剤を配合することにより、硬化性に優れており、良好な強度を示すので、電気・電子部品用として極めて好適である。